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Regional Water Quality Control Board Central Valley Region

Analytical Sensitivity And Detection Limit Terms

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John Swanson

- B.S. Biological Conservation
- 12 years laboratory experience

  Analysis, Quality Assurance, Project Management, Client Services
- 5 years consulting experience

  Project Chemistry, Remedial Investigation, Groundwater Monitoring, QAPPs, SAPs, Reports, Research
- Currently: Environmental Scientist, RWQCB

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Today's Presentation

To Understand the Complexity of Detection Limit Terminology and the Factors That Affect Analytical Sensitivity

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Presentation Objectives

- Discuss the nature of chemical measurements
- Discuss analytical sensitivity and limitations
- Describe detection limit terms and techniques
- Discuss factors that affect sensitivity

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Major Concepts

- Chemicals are all around us
- The amount of a chemical determines if it is a cause for concern
- There are issues of magnitude or scale
- There are limits to analytical sensitivity

EPA MCL for Xylene is 10,000 ug/L,
for 2,3,7,8-TCDD it is 0.00003 ug/L

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Detection Limits

ND ≠ 0

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Chemical Analysis

- Establishes the amount of a chemical parameter in a matrix.
- Amount of chemical parameter / amount of matrix = Concentration
- Common units: mg/L, ug/L, mg/kg, ug/kg, ng/kg, ppm, ppb, ppt, %

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Chemical Concentration Must Be Considered a "Continuum"

- **"Nutri-clean" certified produce**
- **No detected pesticide residues "at all"**
- **"Detected" is the key word**
- **No supermarket or laboratory can prove that their produce contains "zero" pesticide residue**
- **There are limits to what we can "see" or analyze with chemical instruments**

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Chemical Concentration Must Be Considered a "Continuum"

- MCL for Lead = 15 µg/l (ppb)
- MDL = about 1 µg/l = 1 atom lead /10^{12} molecules of water
- At 1 ppb, 20 mL water would contain 10 trillion atoms of lead
- Drinking 1 thousand liters of water at 1 ug/L of lead, you would ingest 1 mg of lead.

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Limits to Analytical Sensitivity: Terms

- **Detection Limit**
- **Quantitation Limit**
- **Reporting Limit**

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Detection Limits Terms

- Detection Limit
- Method Detection Limit (MDL)
  - Defined in 40 CFR, Part 136, App B
- Instrument Detection Limit (IDL)
  - Defined by CLP – Metals only
- Sample Detection Limit

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Quantitation Limit Terms

- Quantitation Limit
- Practical Quantitation Limit (PQL)

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Other Limit Terms

- Contract-required detection limit (CRDL)
- Contract-required quantitation limit (CRQL)
- Limit of Detection (LOD)
- Limit of Quantitation (LOQ)
- Estimated Detection Limit
- Project Required Reporting Limit
- Measurement Reporting Limit (MRL)
- Estimated Maximum Possible Concentration (EMPC)

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MDLs

- Are not quantitative
- Are theoretical estimates
- Change over time
- Are instrument, lab, method, matrix specific
- Are more likely to be affected by matrix interference or blank contamination
- May not represent the true sensitivity of the instrument allowing for false positives or negatives.

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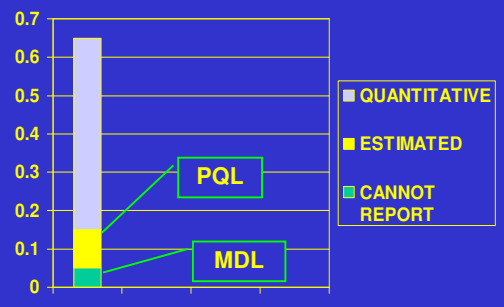
Limits



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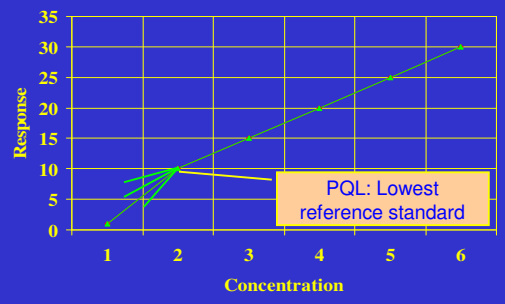
Calibration



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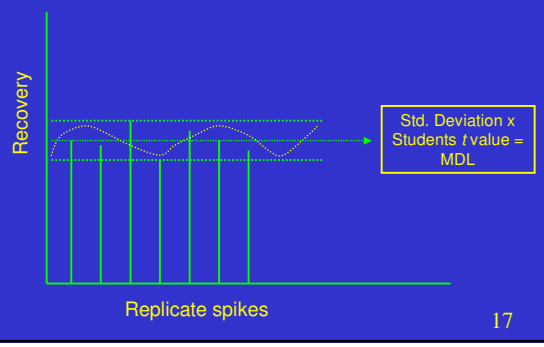
MDL Study



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Example MDL Study

Method: 8330 Matrix: w System: V
Detector: V Unit: ug/L Analysis Date: 12/9/03
Analyst: D.M.Rong Dilution 0.013

Compound	Target	C1	C2	C3	C4	C5	C6	C7	Mean	Stdv	Student's T	MDL	Target/MDL	Mean/Target*100%
													(1 to 10)	(10 to 200)%
1. HMX	0.65	0.7613	0.7558	0.6676	0.781	0.7024	0.8445	0.8327	0.76	0.06	3.14	0.20	3.22949745	117.4771429
2. 1,3,5-TNB	0.65	0.7378	0.7376	0.7349	0.755	0.7097	0.8073	0.7951	0.75	0.04	3.14	0.11	5.89756728	115.9857143
3. RDX	0.65	0.6765	0.7562	0.7613	0.6854	0.6711	0.7539	0.792	0.73	0.05	3.14	0.15	4.22931748	112.0057143
4. 1,3-DNB	0.65	0.6917	0.6962	0.7025	0.7476	0.6926	0.8212	0.8259	0.74	0.06	3.14	0.19	3.41099467	113.8228571
5. 2,4,6-TNT	0.65	0.7779	0.7679	0.7981	0.8334	0.7849	0.8429	0.8927	0.81	0.04	3.14	0.14	4.6416907	125.2285714
6. Tetryl	0.65	0.7257	0.7004	0.7206	0.717	0.6559	0.6538	0.756	0.70	0.04	3.14	0.12	5.44128134	108.36
7.	0.65	0.6819	0.7137	0.6608	0.7656	0.7024	0.8657	0.7669	0.74	0.07	3.14	0.22	2.98508274	113.3371429
8. 2,4-DNT	0.65	0.7544	0.7669	0.8064	0.8115	0.7749	0.8125	0.7974	0.79	0.02	3.14	0.07	8.79813905	121.4085714
9. 2,6-DNT	0.65	0.6579	0.7204	0.7727	0.7552	0.6604	0.7691	0.7726	0.73	0.05	3.14	0.17	3.83103596	112.644
10. 2-Am-4,6-DNT	0.65	0.7258	0.7187	0.7457	0.7703	0.7265	0.786	0.7814	0.75	0.03	3.14	0.09	7.29859345	115.4796286
11. 4-Am-2,6-DNT	0.65	1.0345	1.0368	1.0969	1.0422	1.0597	1.0317	1.0806	1.05	0.03	3.14	0.08	8.12917545	162.2516657
12. 2-NT/4-NT	1.3	1.4577	1.4287	1.5432	1.6314	1.3662	1.7109	1.6459	1.54	0.13	3.14	0.40	3.23660995	118.5057143
13. 3-NT	0.65	0.9991	0.9764	1.0719	1.0283	1.085	1.118	0.9757	1.04	0.06	3.14	0.18	3.67639134	159.4342857

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Example Report

PARAMETERS	RESULTS (ug/L)	RL (ug/L)	MDL (ug/L)
1,1,1-TRICHLOROETHANE	ND	1	.2
1,1,2,2-TETRACHLOROETHANE	ND	1	.3
1,1,2-TRICHLOROETHANE	ND	1	.2
1,1-DICHLOROETHANE	ND	1	.2
1,1-DICHLOROETHENE	ND	1	.2
1,2-DICHLOROETHANE	ND	1	.2
1,2-DICHLOROPROPANE	ND	1	.2
2-BUTANONE (MEK)	ND	10	5
2-HEXANONE	ND	10	1
4-METHYL-2-PENTANONE (MIBK)	ND	10	1
ACETONE	ND	10	2
BENZENE	ND	1	.2
BROMOCHLOROMETHANE	ND	1	.2
BROMODICHLOROMETHANE	ND	1	.2
BROMOFORM	ND	1	.2
BROMOMETHANE	ND	2	.2
CARBON DISULFIDE	ND	1	.2
CARBON TETRACHLORIDE	ND	1	.2
CHLOROBENZENE	ND	1	.2
CHLOROETHANE	ND	2	.2
CHLOROFORM	.48J	1	.2
CHLOROMETHANE	ND	2	.5
CIS-1,2-DICHLOROETHENE	ND	1	.2
CIS-1,3-DICHLOROPROPENE	ND	1	.2

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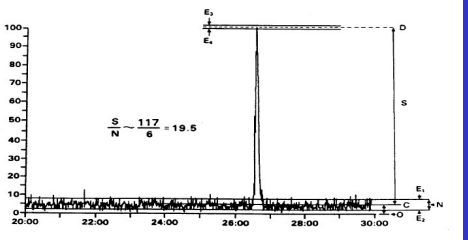
Example Chromatogram



The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal.

NOTE: It is imperative that the instrument interface amplifier electronic zero offset be set high enough so that negative going baseline noise is recorded.

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Factors Affecting Sensitivity

- Method
- Equipment and Reagents
- Matrix interference
- Contamination

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Factors Affecting Sensitivity

- Method Selection

- What's available, approved, accredited, practical

- SW846, Drinking water, Waste water, Experimental, modified or performance-based

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Factors Affecting Sensitivity

More advanced methods can be cost-prohibitive….or not.

Method 200.7 or 6010B, Se MDL = 1-3 µg/l
Method 200.8 or 6020, Se MDL = 0.1-0.2 µg/l
Cost is about $20 for single, $150 for suite

Method 8081A, DDT MDL = 1 ng/L $200
Instrument = $60-100K Standards = $100's
Method 1668, DDT MDL = 0.001 ng/L $800
Instrument = $1,000,000 Standards = $1,000's

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Factors Affecting Sensitivity

- Equipment and Reagents
  - Can add background noise, variability
  - Have greater impact on lower MDLs, and more sensitive methods
- Matrix Interference
  - Can add background noise, or mask signal

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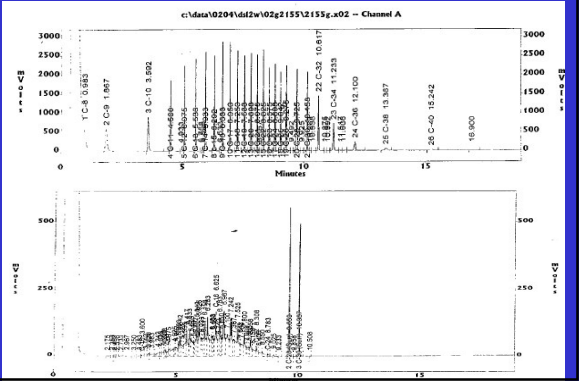
Matrix Interference



Blank Contamination

MDL = 1 ppb, PQL = 4 ppb, Action level = 3 ppb

Sample	MB	FB	SA 1	SA 2	SA 3
Result	2 ppb	3 ppb	ND 1	2 ppb	5 ppb
Sample	SA 4	SA 5			
Result	15 ppb	630 ppb			

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One More Example

Chlorpyrifos

Reg. Limits: Freshwater Aq. Life Protect. = 0.014 µg/l
Cerio LC50 = about 0.08 USEPA IRIS Ref dose 2.1
Lab MDLs: 8141 = 0.08, 0.02, 0.005; GCMS - ??
Sol: 1300 µg/l Half life: months

DDT

Reg Limits: Freshwater Aq. Life Protect. = 0.001 µg/l
USEPA IRIS Ref dose 3.5; Cal Toxics Rule: 0.00059
Lab MDLs 8081 0.01, 0.001; 1668 0.00001 ($$)
Sol: 3 µg/l Half life: decades

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